

**Chapter 24**

- 24-1.** The yellow color comes about because the solution absorbs blue light in the wavelength region 435-480 nm and transmits its complementary color (yellow). The purple color comes about because green radiation (500-560 nm) is absorbed and its complementary color (purple) is transmitted.
- 24-2.** (a) Absorbance  $A$  is the negative logarithm of transmittance  $T$  ( $A = -\log T$ ).
- (b) The molar absorptivity,  $\epsilon$ , is given by  $A/bc$  where  $A$  is the absorbance of a medium having a pathlength of  $b$  cm and an analyte concentration of  $c$  molar. Molar absorptivity has the units of  $\text{L mol}^{-1} \text{cm}^{-1}$ . The absorptivity,  $a$ , is also given by  $A/bc$  where  $A$  is again the absorbance of the medium, but  $b$  may have any specified units of length and  $c$  may have any specified units of concentration.
- 24-3.** Deviations from linearity can occur because of polychromatic radiation, unknown chemical changes such as association or dissociation reactions, stray light, and molecular or ionic interactions at high concentration.
- 24-4.** A real deviation from Beer's law is a deviation due to a real limitation to the law. A real deviation occurs at high concentrations due to molecular or ionic interactions. Other deviations occur because of the imperfect manner in which measurements are made (instrumental deviations) or because of chemical changes that occur with concentration and are unknown to the user.
- 24-5.** Both electronic and vibrational transitions are quantized, that is they occur at specific wavelengths and energies. Electronic transitions are much higher in energy, involving excitation or relaxation of electrons from one orbital to another, while vibrational transitions involve changes in the vibrational frequency of the atoms in a molecule. Both

atoms and molecules can undergo electronic transitions while only molecules can undergo vibrational transitions.

**24-6.**  $\nu = c/\lambda = 3.00 \times 10^{10} \text{ cm s}^{-1}/\lambda(\text{cm}) = (3.00 \times 10^{10}/\lambda) \text{ s}^{-1} = (3.00 \times 10^{10}/\lambda) \text{ Hz}$

(a)  $\nu = 3.00 \times 10^{10} \text{ cm s}^{-1}/(2.65 \text{ \AA} \times 10^{-8} \text{ cm/\AA}) = 1.13 \times 10^{18} \text{ Hz}$

(b)  $\nu = 3.00 \times 10^{10} \text{ cm s}^{-1}/(211.0 \text{ nm} \times 10^{-7} \text{ cm/nm}) = 1.42 \times 10^{15} \text{ Hz}$

(c)  $\nu = 3.00 \times 10^{10} \text{ cm s}^{-1}/(694.3 \text{ nm} \times 10^{-7} \text{ cm/nm}) = 4.32 \times 10^{14} \text{ Hz}$

(d)  $\nu = 3.00 \times 10^{10} \text{ cm s}^{-1}/(10.6 \text{ }\mu\text{m} \times 10^{-4} \text{ cm}/\mu\text{m}) = 2.83 \times 10^{13} \text{ Hz}$

(e)  $\nu = 3.00 \times 10^{10} \text{ cm s}^{-1} / (19.6 \text{ }\mu\text{m} \times 10^{-4} \text{ cm}/\mu\text{m}) = 1.53 \times 10^{13} \text{ Hz}$

(f)  $\nu = 3.00 \times 10^{10} \text{ cm s}^{-1}/1.86 \text{ cm} = 1.61 \times 10^{10} \text{ Hz}$

**24-7.**  $\lambda = c/\nu = 3.00 \times 10^{10} \text{ cm s}^{-1}/\nu (\text{s}^{-1}) = (3.00 \times 10^{10}/\nu) \text{ cm}$

(a)  $\lambda = 3.00 \times 10^{10} \text{ cm s}^{-1}/(118.6 \text{ MHz} \times 10^6 \text{ Hz/MHz}) = 253.0 \text{ cm}$

(b)  $\lambda = 3.00 \times 10^{10} \text{ cm s}^{-1}/(114.10 \text{ kHz} \times 10^3 \text{ kHz/Hz}) = 2.629 \times 10^5 \text{ cm}$

(c)  $\lambda = 3.00 \times 10^{10} \text{ cm s}^{-1}/(105 \text{ MHz} \times 10^6 \text{ Hz/MHz}) = 286 \text{ cm}$

(d)  $\lambda = 1/1210 \text{ cm}^{-1} = 8.264 \times 10^{-4} \text{ cm}$

**24-8.**  $\bar{\nu} = 1/(185 \text{ nm} \times 10^{-7} \text{ cm/nm}) = 5.41 \times 10^4 \text{ cm}^{-1}$  to

$$1/(3000 \times 10^{-7} \text{ cm}) = 3.33 \times 10^3 \text{ cm}^{-1}$$

**24-9.** (a)  $\bar{\nu} = 1/(3 \text{ }\mu\text{m} \times 10^{-4} \text{ cm}/\mu\text{m}) = 3.33 \times 10^3 \text{ cm}^{-1}$  to

$$1/(15 \times 10^{-4} \text{ cm}) = 6.67 \times 10^2 \text{ cm}^{-1}$$

(b)  $\nu = 3.00 \times 10^{10} \text{ cm s}^{-1} \times 3.333 \times 10^3 \text{ cm}^{-1} = 1.00 \times 10^{14} \text{ Hz}$  to

$$3.00 \times 10^{10} \times 6.67 \times 10^2 = 2.00 \times 10^{13} \text{ Hz}$$

**24-10.**  $\nu = c/\lambda = 3.00 \times 10^{10} \text{ cm s}^{-1}/(2.70 \text{ \AA} \times 10^{-8} \text{ cm/\AA}) = 1.11 \times 10^{18} \text{ Hz}$

$$E = h\nu = 6.63 \times 10^{-34} \text{ J s} \times 1.11 \times 10^{18} \text{ s}^{-1} = 7.36 \times 10^{-16} \text{ J}$$

**24-11.**  $\lambda = c/\nu = (3.00 \times 10^{10} \text{ cm s}^{-1}) / (220 \times 10^6 \text{ s}^{-1}) = 136 \text{ cm or } 1.36 \text{ m}$

$$E = h\nu = 6.63 \times 10^{-34} \text{ J s} \times 220 \times 10^6 \text{ s}^{-1} = 1.46 \times 10^{-25} \text{ J}$$

**24-12.** (a)  $\lambda = 589 \text{ nm}/1.35 = 436 \text{ nm}$

(b)  $\lambda = 694.3 \text{ nm}/1.55 = 448 \text{ nm}$

**24-13.** (a)  $\text{ppm}^{-1} \text{ cm}^{-1}$

(b)  $\text{L } \mu\text{g}^{-1} \text{ cm}^{-1}$

(c)  $\%^{-1} \text{ cm}^{-1}$

(d)  $\text{L g}^{-1} \text{ cm}^{-1}$

**24-14.** (a)  $\%T = 100 \times \text{antilog}(-0.0356) = 92.1\%$

Proceeding similarly, we obtain

(b)  $\%T = 12.7$ ; (c)  $\%T = 41.8$ ; (d)  $\%T = 68.1$ ; (e)  $\%T = 32.7$ ; (f)  $\%T = 17.7\%$

**24-15.** (a)  $A = -\log T = -\log (27.2\%/100\%) = 0.565$

Proceeding similarly,

(b)  $A = -\log(0.579) = 0.237$ ; (c)  $A = 0.514$ ; (d)  $A = 1.400$ ; (e)  $A = 1.032$ ; (f)  $A = 0.196$

**24-16.** (a)  $\%T = 100\% \times \text{antilog}(-2 \times 0.0356) = 100\% \times \text{antilog}(-0.0712) = 84.9\%$

Proceeding in the same way,

(b)  $\%T = 1.62\%$ ; (c)  $\%T = 17.5\%$ ; (d)  $\%T = 46.3\%$ ; (e)  $\%T = 10.7\%$ ; (f)  $\%T = 3.12\%$

**24-17.** (a)  $A = -\log T = -\log (0.2272/2) = 0.867$

Proceeding similarly,

(b)  $A = 0.538$ ; (c)  $A = 0.815$ ; (d)  $A = 1.701$ ; (e)  $A = 1.333$ ; (f)  $A = 0.497$

**24-18.** (a)  $\%T = \text{antilog}(-0.172) \times 100\% = 67.3\%$

$$c = A/\varepsilon b = (0.172)/(4.23 \times 10^3 \times 1.00) = 4.07 \times 10^{-5} \text{ M}$$

$$c = 4.07 \times 10^{-5} \frac{\text{mol}}{\text{L}} \times \frac{200 \text{ g}}{\text{mol}} \times \frac{1 \text{ L}}{1000 \text{ g}} \times 10^6 \text{ ppm} = 8.13 \text{ ppm}$$

$$a = A/bc = 0.172/(1.00 \times 8.13) = 0.0211 \text{ cm}^{-1} \text{ ppm}^{-1}$$

Using similar conversions and calculations, we can evaluate the missing quantities

	<i>A</i>	<i>%T</i>	$\varepsilon$ $\text{L mol}^{-1} \text{ cm}^{-1}$	<i>a</i> $\text{cm}^{-1} \text{ ppm}^{-1}$	<i>b</i> $\text{cm}$	<i>c</i> $\text{M}$ $\text{ppm}$	
*(a)	0.172	<b>67.3</b>	$4.23 \times 10^3$	<b>0.0211</b>	1.00	$4.07 \times 10^{-5}$	<b>8.13</b>
(b)	<b>0.348</b>	44.9	<b><math>5.16 \times 10^3</math></b>	0.0258	<b>0.500</b>	$1.35 \times 10^{-4}$	<b>27.0</b>
*(c)	0.520	<b>30.2</b>	$7.95 \times 10^3$	<b>0.0397</b>	1.00	<b><math>6.54 \times 10^{-5}</math></b>	<b>13.1</b>
(d)	<b>0.402</b>	39.6	<b><math>1.83 \times 10^4</math></b>	0.0912	<b>2.50</b>	<b><math>8.80 \times 10^{-6}</math></b>	1.76
*(e)	<b>0.638</b>	<b>23.0</b>	$3.73 \times 10^3$	<b>0.0187</b>	0.100	$1.71 \times 10^{-3}$	<b>342</b>
(f)	<b>0.0778</b>	83.6	<b><math>9.64 \times 10^3</math></b>	<b>0.0483</b>	1.00	$8.07 \times 10^{-6}$	<b>1.61</b>
*(g)	0.798	<b>15.9</b>	<b><math>3.17 \times 10^3</math></b>	<b>0.0158</b>	1.50	<b><math>1.68 \times 10^{-4}</math></b>	33.6
(h)	<b>0.955</b>	11.1	$1.35 \times 10^4$	<b>0.0677</b>	<b>1.00</b>	$7.07 \times 10^{-5}$	<b>14.1</b>
*(i)	<b>1.28</b>	5.23	$9.78 \times 10^3$	<b>0.0489</b>	<b>5.00</b>	<b><math>2.62 \times 10^{-5}</math></b>	5.24
(j)	0.179	<b>66.2</b>	<b><math>2.49 \times 10^3</math></b>	<b>0.0124</b>	1.00	$7.19 \times 10^{-5}$	<b>14.4</b>

**24-19.** molar mass  $\text{KMnO}_4 = 158.03 \text{ g/mol}$

$$c = \frac{4.48 \text{ g KMnO}_4}{10^6 \text{ g soln}} \times \frac{1000 \text{ g soln}}{\text{L}} \times \frac{1 \text{ mol}}{158.03 \text{ g KMnO}_4} = 2.8349 \times 10^{-5} \text{ M}$$

$$A = -\log(0.859) = 0.066$$

$$\varepsilon = A/bc = 0.066/(1.00 \times 2.8349 \times 10^{-5}) = 2.33 \times 10^3 \text{ L mol}^{-1} \text{ cm}^{-1}$$

**24-20.**  $c = \frac{2.25 \text{ g Be(II) complex}}{10^6 \text{ g soln}} \times \frac{1000 \text{ g soln}}{\text{L}} \times \frac{\text{mol}}{166.2 \text{ g Be(II)complex}} = 1.354 \times 10^{-5} \text{ M}$

$$A = -\log(37.5\%/100\%) = 0.426$$

$$\varepsilon = A/bc = 0.426/1.354 \times 10^{-5} = 3.15 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$$

**24-21.** (a)  $A = 7.00 \times 10^3 \text{ L mol}^{-1} \text{ cm}^{-1} \times 1.00 \text{ cm} \times 3.40 \times 10^{-5} \text{ mol L}^{-1} = 0.238$

$$(b) A = 7.00 \times 10^3 \times 1.00 \times 2 \times 3.40 \times 10^{-5} = 0.476$$

$$(c) \text{ For part (a), } T = \text{antilog}(-0.238) = 0.578$$

$$\text{For part (b), } T = \text{antilog}(-0.476) = 0.334$$

$$(d) A = -\log(T) = -\log(0.578/2) = 0.539$$

**24-22.**

$$c = \frac{4.33 \cancel{\text{ g Fe}}}{10^6 \cancel{\text{ g soln}}} \times \frac{1000 \cancel{\text{ g soln}}}{\text{L}} \times \frac{\cancel{\text{ mol Fe}}}{55.847 \cancel{\text{ g Fe}}} \times \frac{1 \text{ mol FeSCN}^{2+}}{\cancel{\text{ mol Fe}}} \times \frac{5.00 \text{ mL}}{50.00 \text{ mL}}$$

$$= 7.75 \times 10^{-6} \text{ M}$$

$$A = 7.00 \times 10^3 \times 2.50 \times 7.75 \times 10^{-6} = 0.136$$

$$\mathbf{24-23.} (a) A = 9.32 \times 10^3 \text{ L mol}^{-1} \text{ cm}^{-1} \times 1.00 \text{ cm} \times 5.67 \times 10^{-5} \text{ mol L}^{-1} = 0.528$$

$$(b) \%T = 100 \times \text{antilog}(-0.528) = 29.6\%$$

$$(c) c = A/\epsilon b = 0.528/(9.32 \times 10^3 \text{ L mol}^{-1} \text{ cm}^{-1} \times 2.50 \text{ cm}) = 2.27 \times 10^{-5} \text{ M}$$

$$\mathbf{24-24.} (a) A = 7000 \text{ L mol}^{-1} \text{ cm}^{-1} \times 1.00 \text{ cm} \times 6.17 \times 10^{-5} \text{ mol L}^{-1} = 0.439$$

$$(b) \%T = 100 \times \text{antilog}(-0.439) = 36.4\%$$

$$(c) c = A/\epsilon b = 0.439/(7000 \text{ L mol}^{-1} \text{ cm}^{-1} \times 5.00 \text{ cm}) = 1.25 \times 10^{-5} \text{ M}$$

$$(d) b = A/\epsilon c = 0.439/(7000 \text{ L mol}^{-1} \text{ cm}^{-1} \times 3.13 \times 10^{-5} \text{ mol L}^{-1}) = 2.00 \text{ cm}$$

$$\mathbf{24-25.} 2.10 = -\log(P/P_0) \quad P/P_0 = 0.0079433$$

$$P = 0.007943 P_0$$

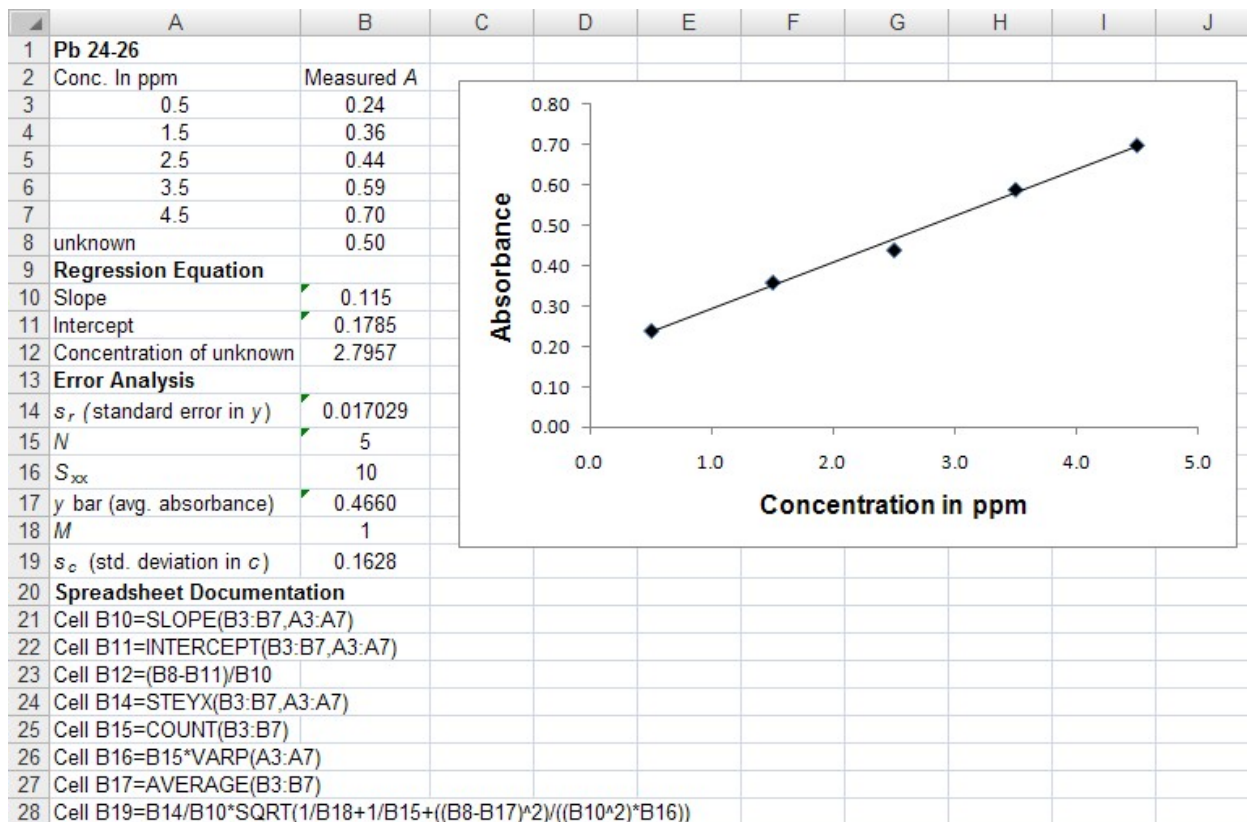
$$P_s/P_0 = 0.0075$$

$$P_s = 0.0075 P_0$$

$$A' = \left( \frac{P_0 + P_s}{P + P_s} \right) = \log \left( \frac{P_0 + 0.0075 P_0}{0.007943 P_0 + 0.0075 P_0} \right) = \log \left( \frac{1.0075 P_0}{0.015443 P_0} \right) = \log(65.2139)$$

$$= 1.81$$

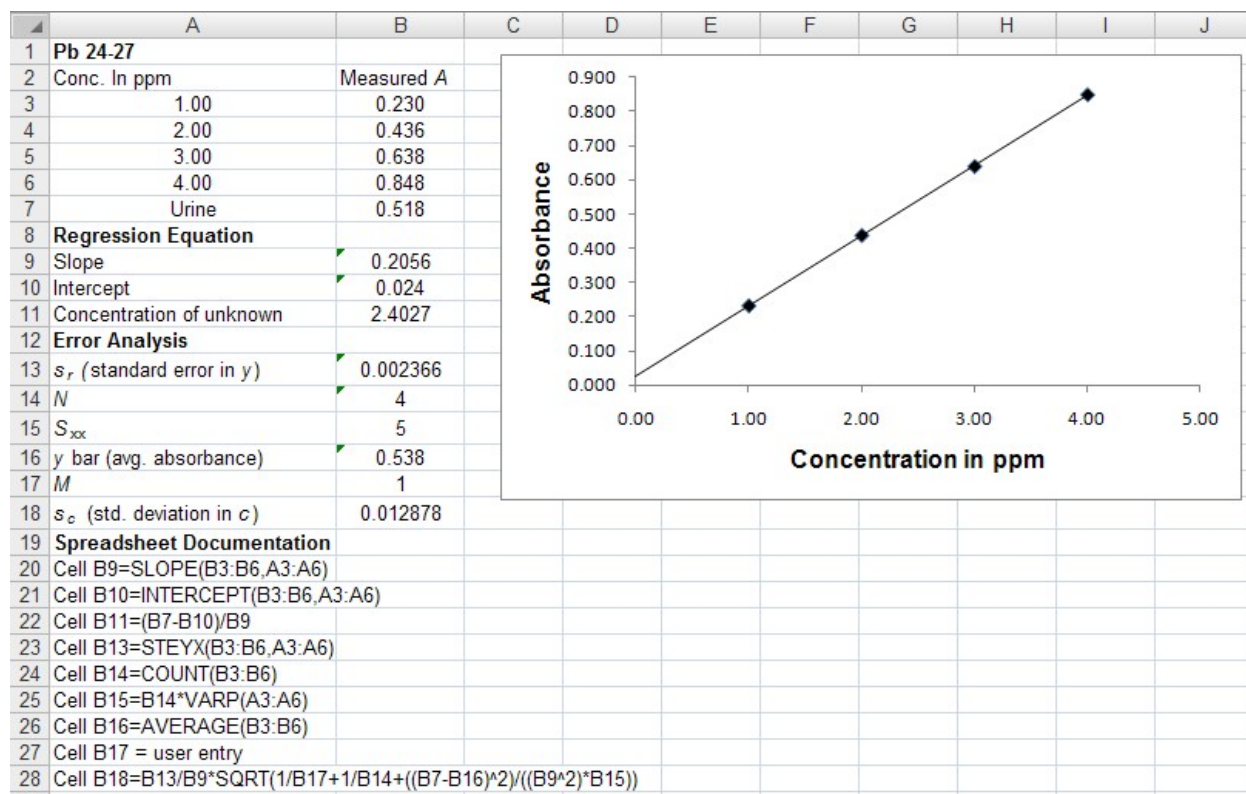
$$\text{Error} = [(1.81 - 2.10)/2.10] \times \% 100 = -13.6\%$$

**24-26.**

Rounding to keep only significant figures, we have

$$c_{\text{unk}} = 2.8 \pm 0.2 \text{ ppm}$$

## 24-27. (a)

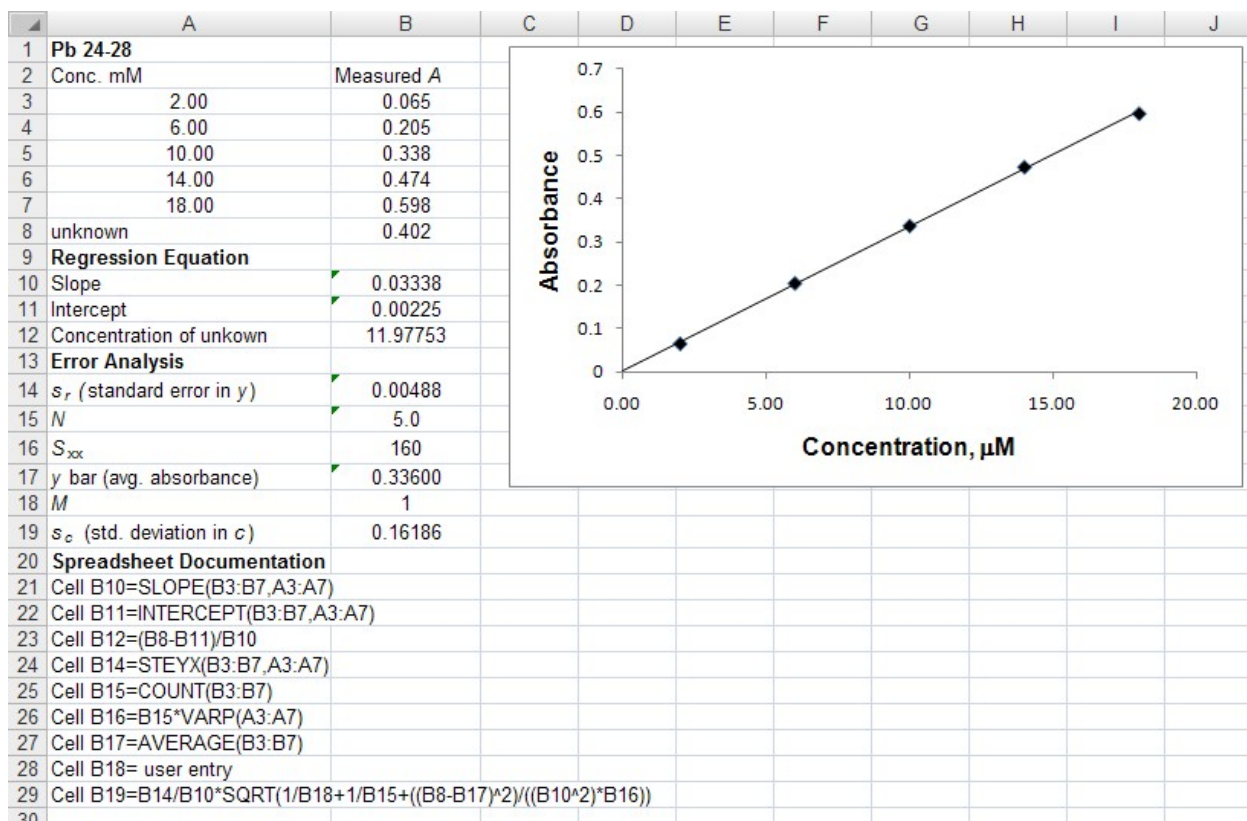


$$(b) \text{ mass P} = 1123 \text{ mL} \times 1122 \frac{\text{mL}}{\text{L}} \times \frac{2.4 \text{ mg P}}{1000 \frac{\text{mL}}{\text{L}}} \times \frac{50.0 \frac{\text{mL}}{\text{L}}}{1.00 \frac{\text{mL}}{\text{L}}} = 135 \text{ mg P}$$

$$(c) \text{ conc. PO}_4^{3-} =$$

$$\frac{2.4 \text{ mg P}}{\text{L}} \times \frac{50.0 \frac{\text{mL}}{\text{L}}}{1 \frac{\text{mL}}{\text{L}}} \times \frac{1 \text{ mmol P}}{30.9738 \frac{\text{mg P}}{\text{mmol P}}} \times \frac{1 \text{ mmol PO}_4^{3-}}{1 \text{ mmol P}} = 3.87 \text{ mM}$$

## 24-28.



Rounding to keep only significant figures

$$c_{\text{unk}} = 12.0 \pm 0.2 \mu\text{M}$$

**24-29.**  $[\text{Cr}_2\text{O}_7^{2-}]/\{[\text{CrO}_4^{2-}][\text{H}^+]^2 = 4.2 \times 10^{14}$

$$[\text{H}^+] = \text{antilog}(-5.60) = 2.51 \times 10^{-6}$$

$$[\text{Cr}_2\text{O}_7^{2-}] = c_{\text{K}_2\text{Cr}_2\text{O}_7} - [\text{CrO}_4^{2-}]/2$$

$$\frac{c_{\text{K}_2\text{Cr}_2\text{O}_7} - 0.500[\text{CrO}_4^{2-}]}{[\text{CrO}_4^{2-}]^2 \times (2.51 \times 10^{-6})^2} = 4.2 \times 10^{14}$$

$$c_{\text{K}_2\text{Cr}_2\text{O}_7} - 0.500 [\text{CrO}_4^{2-}] = 2.65 \times 10^3 [\text{CrO}_4^{2-}]^2$$

$$[\text{CrO}_4^{2-}]^2 + 1.887 \times 10^{-4} [\text{CrO}_4^{2-}] - 3.774 \times 10^{-4} c_{\text{K}_2\text{Cr}_2\text{O}_7} = 0$$

When  $c_{\text{K}_2\text{Cr}_2\text{O}_7} = 4.00 \times 10^{-4}$

$$[\text{CrO}_4^{2-}]^2 + 1.887 \times 10^{-4} [\text{CrO}_4^{2-}] - 1.510 \times 10^{-7} = 0$$

$$[\text{CrO}_4^{2-}] = 3.055 \times 10^{-4} \text{ M}$$

$$[\text{Cr}_2\text{O}_7^{2-}] = 4.00 \times 10^{-4} - 3.055 \times 10^{-4} / 2 = 2.473 \times 10^{-4}$$

$$A_{345} = 1.84 \times 10^3 \times 3.055 \times 10^{-4} + 10.7 \times 10^2 \times 2.473 \times 10^{-4} = 0.827$$

$$A_{370} = 4.81 \times 10^3 \times 3.055 \times 10^{-4} + 7.28 \times 10^2 \times 2.473 \times 10^{-4} = 1.649$$

$$A_{400} = 1.88 \times 10^3 \times 3.055 \times 10^{-4} + 1.89 \times 10^2 \times 2.473 \times 10^{-4} = 0.621$$

Proceeding in the same way, we obtain

$c_{\text{K}_2\text{Cr}_2\text{O}_7^{2-}}$	$[\text{CrO}_4^{2-}]$	$[\text{Cr}_2\text{O}_7^{2-}]$	$A_{345}$	$A_{370}$	$A_{400}$
$4.00 \times 10^{-4}$	$3.055 \times 10^{-4}$	$2.473 \times 10^{-4}$	0.827	1.649	0.621
$3.00 \times 10^{-4}$	$2.551 \times 10^{-4}$	$1.725 \times 10^{-4}$	0.654	1.353	0.512
$2.00 \times 10^{-4}$	$1.961 \times 10^{-4}$	$1.019 \times 10^{-4}$	0.470	1.018	0.388
$1.00 \times 10^{-4}$	$1.216 \times 10^{-4}$	$3.920 \times 10^{-4}$	0.266	0.613	0.236
0.0	0.0	0.0	0.000	0.000	0.000

Plotting these data clearly shows the deviations from linearity that occur

